



Automatic device for continuous measurement of potential distribution and acid stratification in flooded lead-acid batteries

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H I G H L I G H T S

- In situ measurement of acid stratification and potential distribution.
- Detailed description of inhomogeneous ageing of flooded SLI.
- Measurement of electrochemical active regions.

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A microcontroller-based device has been developed for continuous measurement of current distribution and acid stratification in commercial flooded lead-acid batteries. Acid density at four different levels is measured using micro reference cells and the current density is determined from potential drops along the grid. The measurement method, the full device and measurement results are presented and discussed.

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1. Introduction

Having a look at flooded lead-acid batteries' behaviour, it becomes obvious that acid stratification is a dominant factor for ageing processes and rapid reversible capacity loss in real-world-applications [1–3]. Acid stratification influences for example the local depth of discharge (DOD) in the cell caused by inhomogeneous current distribution, resulting in inhomogeneous ageing as well [4,5]. In addition, this causes many problems for battery diagnostics. A strong dependency of the dynamic charge acceptance (DCA) during micro-cycling in conventional and micro-hybrid vehicles on current distribution and thus on acid stratification has been reported [5]. Many factors affect the occurrence and the strength of acid-stratification, such as current rate,

temperature and deep discharges. The resulting inhomogeneous current distribution depends strongly on the current rates during charging and discharging. Models and measurements have shown that the lower part of the electrode reaches states of charge which are well below the average SOC in the cell [6]. This is known as a frequent cause of failure in lead-acid batteries. Post-mortem analysis on flooded batteries from partial state-of-charge cycling shows a strong sulphation in the lower part of the electrodes, mainly in the negative electrode, which is in accordance with the assumption of lower SOC's in these parts of the cell.

The aim of this work is the development and validation of an in situ measurement method for detecting the potential distribution in the electrode and the vertical acid stratification. This method allows further measurements concerning the interaction of acid-stratification and current distribution in future. Results can be used e.g. for diagnostics of flooded lead-acid batteries, life time prediction under real life conditions, development of measures for removal of acid stratification in the field, and finally could help

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developing improved lead-acid batteries with reduced acid stratification.

An alternative to the presented measurement principle is a portable density metre, which is not applicable for in situ measurements. Other in situ measurement principles are based e.g. on measuring the refractive index by using optical fibres [7,8]. The method presented in this article by using micro reference cells is applicable for in situ measurements as well. Another advantage is the small size of the sensors compared to those based on measuring the refractive index. This allows also measurements in SLI batteries. The hardware for data acquisition can be used for mobile applications, so that e.g. measurement of acid densities in an SLI battery of a vehicle during normal operation is possible.

Modelling and investigations of current distribution over the electrode has been already studied [9–13].

Measurements in this work have been performed only on commercial flooded SLI batteries. Nevertheless, the concepts are usable in a similar way for stationary and industrial lead-acid batteries.

2. Experimental set-up

Working principle and experimental set-up for acid density and current distribution measurement are presented separately in the next two sections. The following section presents a simple combined model for both measurements. Section 2.4 deals with the microcontroller based data acquisition tool for both measurement principles.

2.1. Acid density measurement

Acid stratification is measured in one cell by four single measurements of the acid density at different positions. These positions are at different heights in the cell. The horizontal acid gradients are not measured, assuming a rapid horizontal diffusion process resulting in small acid gradients within a horizontal level. One sensor is above the electrodes and the other three next to the electrodes. For better comparison with a simulation model [14] – as has been done in Ref. [5], the four positions (see also Fig. 5) are chosen as follows (with height h of the electrode):

- one in the middle of the lowest third of the electrodes, so $h/6$ from the electrodes' bottom
- one in the middle of the electrodes $h/2$
- one in the middle of the upper third of the electrodes, so $h * 5/6$ from the electrodes' bottom
- one in the electrolyte above the electrodes

Each sensor consists of two isolated lead wires (1 mm diameter, 99.9% metals basis, Alfa Aesar) working as a micro reference cell. A brand new sensor has to be charged with a high overvoltage to build up active material following a corrosion process. Duration and current rate are important factors for the reliability of the sensors in the following measurements. Charging each single wire against the corresponding electrode of an industrial flooded lead-acid battery has a positive influence on its behaviour in later measurements. The procedure is similar to the formation of Planté cells.

The four sensors are produced identically with exception to their length. Fig. 1 shows one complete set of sensors. Each sensor is placed through a hole drilled at the outside margin of the battery's top cover.

Acid density cannot be measured directly with this method; but the sensors work like a usual lead-acid cell: the open circuit voltage (OCV) measured between anode and cathode depends strongly on

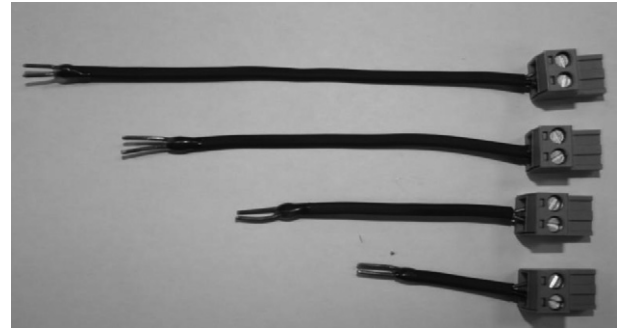


Fig. 1. Set of four acid density sensors.

the acid concentration. One can obtain the acid density from the acid concentration by calculation.

From the voltage measurement, acid density can be determined. First of all the dependency of the voltage from molality can be derived using the following equation [15]:

$$\begin{aligned}
 U = & 1922.8 \text{ mV} + 147.519 \text{ mV} * \log\left(m * \frac{\text{kg}}{\text{mol}}\right) \\
 & + 63.552 \text{ mV} * \log^2\left(m * \frac{\text{kg}}{\text{mol}}\right) \\
 & + 73.772 \text{ mV} * \log^3\left(m * \frac{\text{kg}}{\text{mol}}\right) \\
 & + 33.612 \text{ mV} * \log^4\left(m * \frac{\text{kg}}{\text{mol}}\right)
 \end{aligned} \quad (2.1)$$

where U is the voltage in mV and m is the molality of the sulphuric acid in mol kg^{-1} . The dependency of molality and density is described in Ref. [15] as well, so that one can obtain an expression for calculating the density in dependency of the voltage. Fig. 2 shows the dependency of the OCV on the acid density calculated with equation (2.1).

The often used empirical formula [16]

$$\frac{U}{[\text{V}]} = \frac{\rho}{[\text{g} * \text{cm}^{-3}]} + 0.84 \quad (2.2)$$

is also displayed in this figure for comparison.

The formation of mixed potentials caused by self discharge effects is not taken into account for the calculation of the acid density. The error caused by this will be neglected because grid alloys without antimony are used for the experiments and therefore the gassing reaction current will be relatively low.

Acid stratification can be determined by measuring the OCV of the micro reference cells at different levels in the electrolyte. But these cells – as mentioned before – are quite similar to lead-acid batteries and show the same behaviour. Therefore, also self-discharge occurs so that the sensors have to be recharged periodically. During the recharging period no valid signal for the acid concentration can be obtained. Another disadvantage is the occurring overvoltage after each full charge. This overvoltage has to decay before the correct OCV can be measured for calculating the acid density. Fig. 3 shows the raw data of such a measurement for a single sensor. The sensor was placed in a cell of a commercial starter battery in a climate chamber at 25 °C. A rest period (for the battery) without charge or discharge current is shown in this figure, so that changes of acid density are only possible due to diffusion processes.

The measurement can be divided into three parts (I, II and III) as can be seen in the figure. Each cyclic charging period for 2 h (I) is followed by a decay time of the resulting overvoltage; this decay time (II) varies with each sensor and the acid concentration

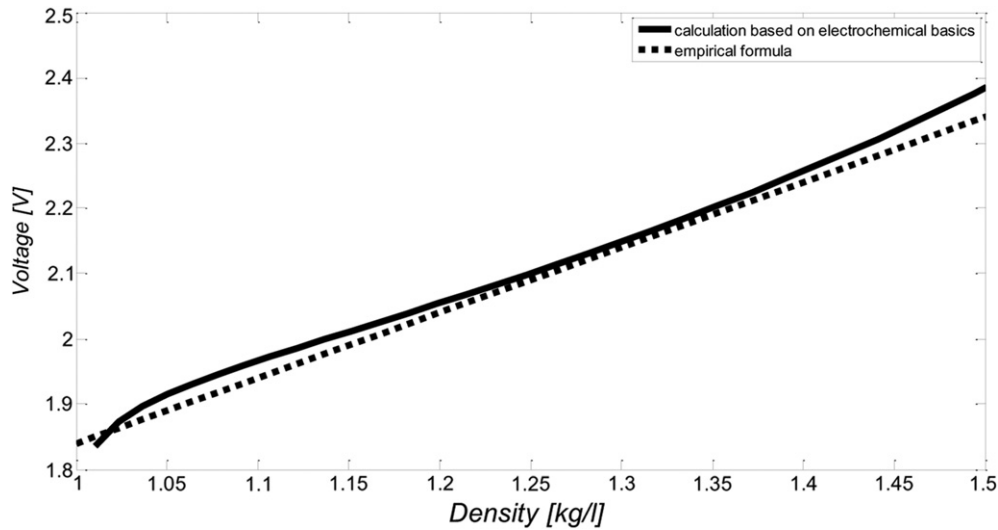


Fig. 2. Dependency of OCV on density in a typical range for lead-acid batteries at a temperature of 25 °C.

between both sensors' electrodes. These two parts (I and II) together are a dead-time for the measurement and have to be considered when setting up a measurement. In part III the usable measurement takes place. A slight decrease of the OCV remains due to the self-discharge of the sensors. This self-discharge in each measuring period has to be accepted and considered as an error for the calculated densities. E.g. a decrease of 13 mV (from 2.109 V to 2.096 V) can be seen for the measuring period between $t = 12.8$ h and $t = 16$ h; this corresponds to an absolute error of $\Delta\rho = 0.013 \text{ kg l}^{-1}$. One should keep this error in mind, but it is acceptable for this application, because much larger changes in acid densities up to 0.350 kg l^{-1} can be observed in the experiments.

Periods of 2 h of charging followed by 4 h of measurement have turned out to be a good compromise between measurement and dead time.

The measurement current of the device has been determined. The current is +5.98 pA, this corresponds to a charge of about 86 nA-s during one single measuring period of 4 h. The capacity of the sensor is about 0.7 A-s (for a 7 mm long active region using a wire with a diameter of 1 mm and active material surface of

50 μm). So there is a difference of about 6 orders of magnitude between the capacity of the sensor and the capacity change caused by the measurement device. The influence of the measurement device on the OCV measurement is therefore negligible.

It is not fully understood yet, which process causes the rapid self discharge. This will be investigated in more detail in the future, but is not affecting the functionality of the system if operated as described beforehand.

2.2. Current distribution measurement

A direct current measurement in the electrodes' grid is not possible, but not necessary either for investigation of the current distribution. It is sufficient to have knowledge about the relative current distribution over the height of the electrodes.

A homogeneous resistance along the grid is assumed; corrosion is negligible for the duration of the experiment. The location of the measurement points was chosen to be easily comparable to the simulation and the acid stratification results: so the vertical edge was divided symmetrically into three parts. In order to access the

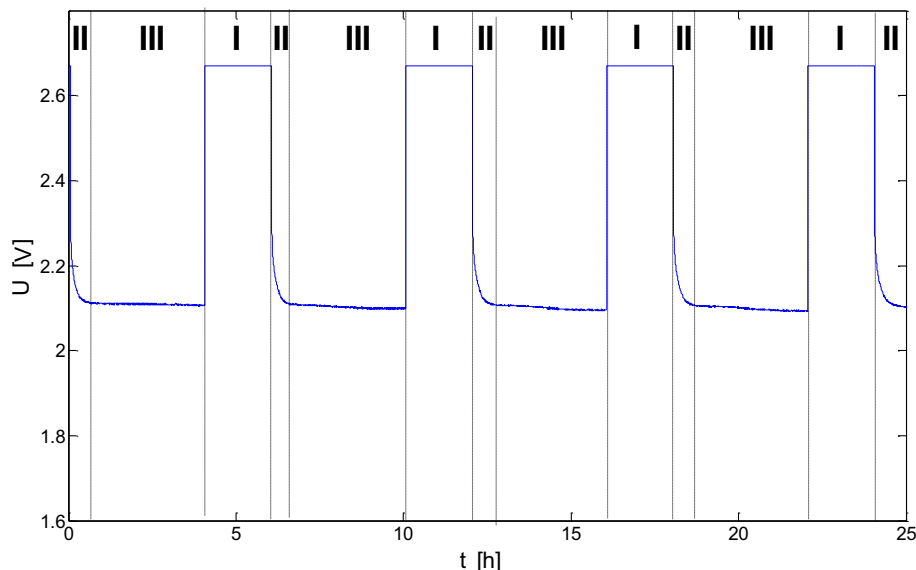


Fig. 3. Voltage measurement of a single sensor (I: charging and regeneration, II: decay of overvoltage, III: usable for measurement).

grid, the battery and the separators have to be opened and a small lead wire is welded to the grid. Only the negative electrode was contacted for measurements, because lead corrodes if it is contacted to the positive potential of the lead-acid battery.

Fig. 4 shows a photo of such a connection to a brand-new grid. Afterwards the battery is sealed again and the lead wires are connected to the data acquisition device.

Four of these connections are dividing the grid in the same top, middle and bottom zones that are used for the electrolyte density measurement, too. The reference potential measurement is a fifth lead wire connected to the strap.

2.3. Combined model and equivalent circuit diagram

A schematic of the measurement principle for acid stratification and current distribution is shown in Fig. 5. The sensors S_1 – S_4 for acid density are placed next to the electrodes and in the middle of each zone. The lead-connections C_1 – C_4 for the potential measurements limit the three zones in which the acid density can be measured; each voltage is measured against C_0 , which is connected to the strap.

A first very simple combined model for both measurements is necessary for interpretation of the acid stratification and current distribution results and especially for understanding the interaction of both processes.

Fig. 6 shows the equivalent circuit diagram [17] on which the interpretation of the experimental results is based. The plates are divided symmetrically in three parts, each represented by a horizontal subcircuit.

The elements in this equivalent circuit diagram are representing the following physical effects [15,17]:

- R_a , R_b and R_c represent the grid resistance of positive and negative electrodes in each part of the electrode. R_a includes additionally the resistance of the plate connectors and the poles.
- R_1 , R_2 and R_3 represent the sum of all Ohmic resistances in the horizontal direction including the electrolyte resistance depending on acid density and temperature, the active material resistance (depending on the state of charge and temperature), and the corrosion layer between grid and active material.
- $C_{RC,1}$, $C_{RC,2}$ and $C_{RC,3}$ represent double layer capacitances.
- $R_{RC,1}$, $R_{RC,2}$ and $R_{RC,3}$ representing the reaction resistance (kinetics) given by the Butler–Volmer–Equation and therefore depending on the current, local state of charge and temperature [18].
- $U_{SP,1}$, $U_{SP,2}$, $U_{SP,3}$ represent the local OCV which depend on the local acid concentration.
- $U_{RC,1}$, $U_{RC,2}$, $U_{RC,3}$ are just describing the voltage drop of the electrochemical charge/discharge reaction. They can be used instead the $R_{RC}||C_{RC}$ elements.

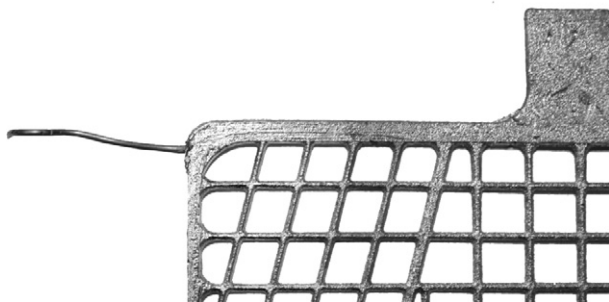


Fig. 4. Connection of a lead wire to the grid.

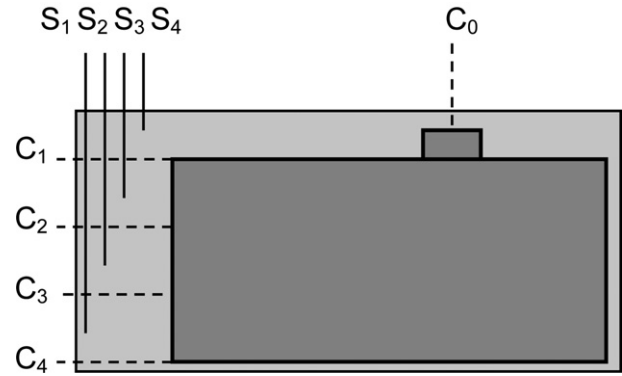


Fig. 5. Schematic of the measurement principle.

This model represents the interaction between local acid density and current distribution inside the battery cell. As one can see, $U_{SP,1}$, $U_{SP,2}$, $U_{SP,3}$ and R_1 , R_2 , R_3 depend on the local acid density. At the same time these elements influence the current distribution, so that inhomogeneous acid density distribution causes inhomogeneous current distribution and vice versa.

The presented measurement – as already mentioned – is not able to measure the current, but it can explain the current distribution and therefore the current for electrochemical reaction in certain regions. This allows general time and spatially resolved conclusions about electrochemical reaction rate. Horizontal equipotential lines are assumed to simplify matters. Equipotential lines in reality depend on the geometry of the grid. A simulation of the potential distribution for different grid geometries can be found in Ref. [19].

The following considerations are used for interpretation of the measurements.

Figs. 7 and 8 illustrate two examples of different behaviour assuming horizontal equipotential lines and current I_0 at the top of the electrode. The current intensity decreases linearly with distance in the first example (Fig. 7). The current applied to

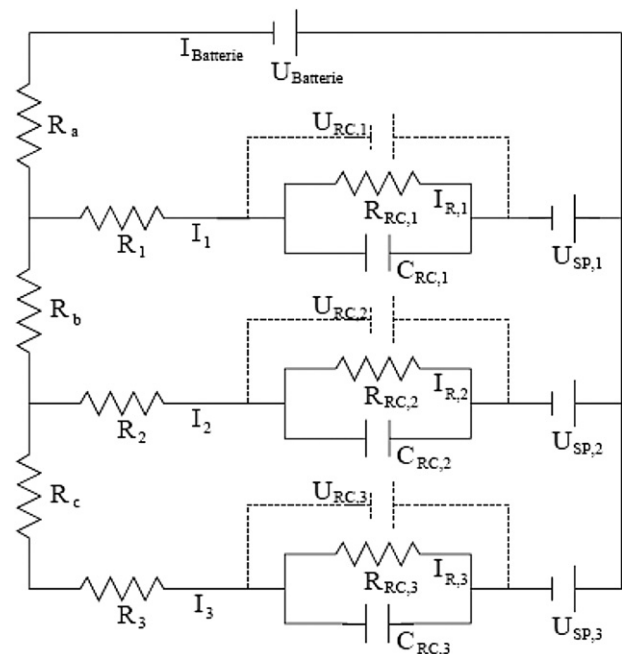


Fig. 6. Equivalent circuit diagram [17].



Fig. 7. Current distribution in the grid for homogeneous electrochemical reaction.

electrochemical reaction is constant and does not depend on the level. A homogeneous reaction (either a charging or a discharging reaction) along the electrode, which is equal to a reaction current of one third of the initial current in each region, can be determined.

Fig. 8 shows another example: initial current I_0 is constant in the upper half of the electrode so that there is no reaction current leaving the electrode in that region. The current decreases linearly in the lower part, so that there is a constant reaction current like in the first example. This means for the different regions:

- upper region: there is no reaction current and consequently no electrochemical reactions in this region. The region is inactive.
- middle region: there is no reaction current in the upper half but a constant one in the lower part. The region has active and inactive parts. One third of the whole electrochemical reaction takes place in this region.
- lower region: there is a constant reaction current in this part. Two third of the whole electrochemical reaction takes place in this region.

So Fig. 8 shows the interpretation of the measurement results for an electrode which is inactive in the upper half and all electrochemical reactions take place in the lower part (in this region the reaction is homogeneous).

2.4. Data acquisition

Data acquisition for both measurements is carried out by a microcontroller-based device. Each device can be equipped with up to six modules, each of those measuring one potential difference. The core of this device is an Atmel ATmega32 microcontroller with internal analogue to digital converter (ADC). It works with 10 bit resolution and an integrated signal conditioning circuit, based on a high-quality instrumentation amplifier, which lowers the

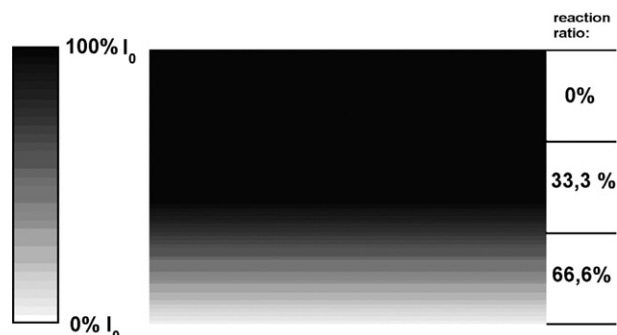


Fig. 8. Current distribution in the grid for inhomogeneous electrochemical reaction.

input bias current to less than 10 pA. The absolute resolution depends on the measuring range:

- OCV measurements for determining the acid density are limited to a range of about 1.55–2.55 V. The resulting absolute resolution is ca. 1 mV.
- potential measurements for measuring the current distribution are limited to –25 mV to 25 mV. Absolute resolution is about 50 μ V.

Data can be stored on a commercial SD memory card and can also be logged by a USB interface simultaneously using a PC. The device is also able to charge each sensor with a certain voltage, which is necessary for the acid density measurement.

3. Experimental results

The aim of the experiments is a validation of both measurement methods. In general, there are different timescales for the two effects. While the current distribution changes instantaneously during the operation of the battery, acid stratification is a phenomenon with a long time constant in the range of minutes to hours. So the validation measurements were separated in two different experiments.

3.1. Validation measurement for the acid stratification determination

A commercial SLI starter battery with 60 Ah rated capacity C_{20} used for OEMs (T6 size) was used for this experiment with a constant temperature in the climate chamber at 25 °C.

The following measurement, starting in a fully charged and unstratified state of the battery, was conducted for validation of the measurement principle and hardware as described before:

- discharge with 4 I_{20} until voltage is less than 1.7 V per cell
- rest period of 5 h
- charge with 4 I_{20} until voltage reaches 2.6 V per cell
- charge at 2.6 V per cell for 1 h
- charge at 2.4 V per cell for 5 h
- rest period of 4 h

This procedure was repeated three times.

The results of this measurement can be seen in Fig. 9. Acid density is shown on the left ordinate, while the right one shows the cell voltage to illustrate, which step in the cycling regime is going on. The signals of the sensors during the dead times as well as during the decays of the overvoltage are not shown.

The measurement starts (I) with a nearly unstratified battery and a rest period. Homogeneous electrolyte was achieved by bubbling nitrogen gas through the battery for a few minutes. As expected, acid density decreases at all four levels during discharge (II). After discharging, acid density in the different heights is already different as can be seen in the rest period of 5 h (III). Acid density in the lower part is higher than in the rest of the cell. This is expected due to the inhomogeneous current distribution in the cell caused by the grid resistance. During charging the average acid density increases and beside this an extensive acid stratification with a difference of about 0.2 kg l^{-1} between upper and lower part (IV) can be observed. The change of the acid densities during the charging process cannot be seen in detail due to the dead time of the sensors. A second charging starts at about $t = 34$ h. The first part is a charge with constant current 4 I_{20} and increasing voltage up to 2.6 V per cell. An increasing acid density between the electrodes can be observed. The acid density above the electrodes is nearly

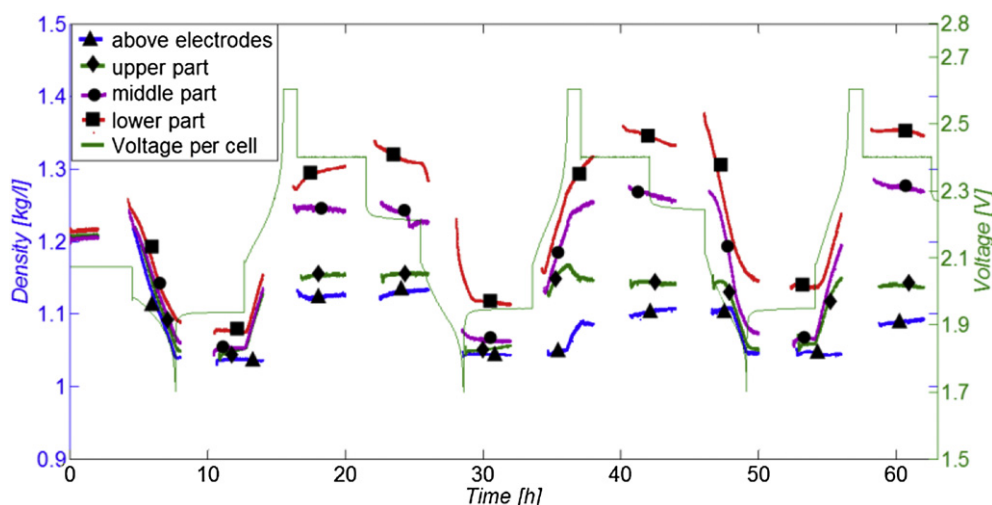


Fig. 9. Results of the acid stratification measurement.

unaffected, because diffusion takes place on greater timescales. Further charging leads to increasing voltage and the gassing mixes up the electrolyte (VI). This results in a sharp increase of acid density above the electrodes. Acid density in the upper part between the electrodes decreases although charging takes place. The density in the middle and lower parts increases more slowly than before.

The measurement results are in good agreement with the expected behaviour of acid stratification. Effects like increasing acid density during charging, decreasing acid density during discharging, growing stratification, destratification and gassing can be observed and thus the measurement method has proven to be a valuable tool for observing changes in acid density.

Another measurement consisting of a discharge followed by a rest period and a charge process is shown in Fig. 10. At about $t = 46.5$ h the battery is discharged. Acid density in the lower region decreases; the decrease of acid density in the upper part starts later (at about $t = 47.5$ h) and indicates that the discharging takes place inhomogeneously and starts in the lower regions. This is in compliance with the theory shown in the equivalent circuit diagram in Fig. 6. Discharging starts in a stratified state; there is

a higher acid density in the lower regions which implies for the theoretic model:

$$U_{SP1} < U_{SP2} < U_{SP3} \text{ and } R_1 > R_2 > R_3$$

The current distribution becomes inhomogeneous and the amount of current taking part at discharge reactions increases towards the bottom of the electrode.

During the rest period after discharging, the acid density distribution is inhomogeneous. Acid density in the lower part is higher than in the middle and upper parts. Charging starts at about $t = 54$ h; the development of the acid density is as follows: $U_{SP1} < U_{SP2} < U_{SP3}$ and $R_1 > R_2 > R_3$ are valid again. But the sign of the current has changed. So the current going into electrochemical charge process is higher if the acid density is lower. In this case charging starts in the upper regions and increasing acid densities in the middle and upper regions are detected. In contrast to this, the acid density in the lower region is nearly constant in the first minutes of the charging process. The acid density above the electrodes does not change because gassing is negligible for these voltages ($t < 56$ h). The acid density for higher voltages during

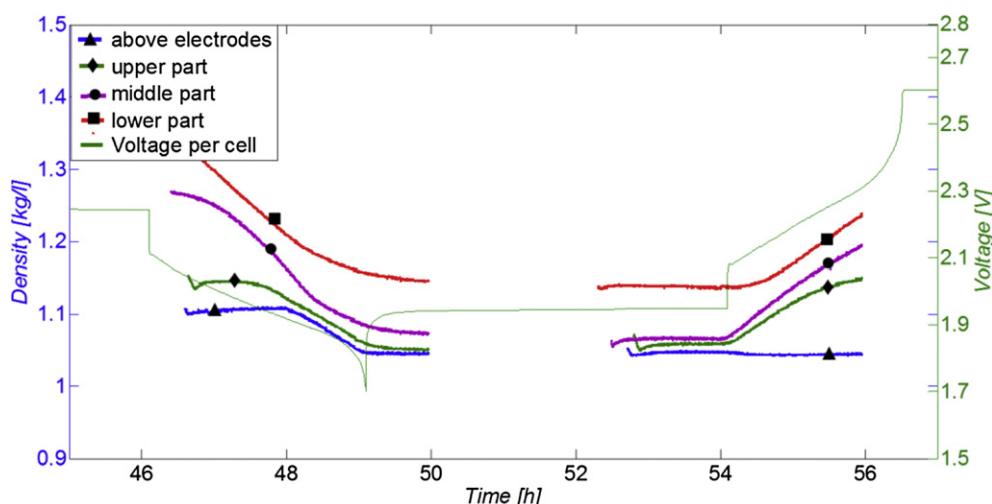


Fig. 10. Acid density at different levels during charge and discharge.

charging was not measured in this case because of a dead time of the sensors due to refreshment.

In its current state, the technique allows for continuous in situ monitoring of acid concentration and their evolution during battery operation. However, measurement errors (particularly potential drift) and frequent need for recharge prevent a precise concentration measurement. An improved version with reduced errors and extended “active” measurement periods is under development.

3.2. Validation measurement for the current distribution

Changes of the current distribution can occur on short time-scales and therefore micro-cycles are used for validation. The experimental set-up as described above was used.

The fully charged battery was discharged to 0% SOC and afterwards charged to 70% SOC as described in Ref. [5] for pre-conditioning. Results of simulation and measurements are in good agreement. Pulses with 20 I_{20} (here 60 A) and 1% cycle depth limited by 14.4 V were used. One thousand of these discharge/charge pulses were applied to the battery. The voltage drops between strap and the four different levels were logged. The voltage drops of the first and last micro-cycles of this measurement will be compared in the following.

Fig. 11 shows the voltage drop of the first micro-cycles after a rest period. The figure represents the general expected results: The voltage drop is highest in the lowest part of the electrode and lowest in the upper part of the electrodes.

Another kind of illustration is helpful for the interpretation. The difference of each voltage drop to $U_{C0}-U_{C1}$ is displayed in Fig. 12.

The differences are:

- $\Delta U_2 = (U_{C0} - U_{C2}) - (U_{C0} - U_{C1})$
- $\Delta U_3 = (U_{C0} - U_{C3}) - (U_{C0} - U_{C1})$
- $\Delta U_4 = (U_{C0} - U_{C4}) - (U_{C0} - U_{C1})$

First of all Fig. 11 shows that the voltage drop decreases with increasing duration of the pulse during charging, whereas the voltage distribution remains mainly constant during discharging. The main reason for the voltage drop during charging is the limited charge acceptance of the battery. The battery voltage is limited to 14.4 V by reducing the current and hence reducing potential drops. As the pulse is limited by the Ah amount, the duration is longer than during discharging (36 s).

However, it is interesting to have a closer look at Fig. 12. The voltage limitation during charging can be seen more extensively in the lower part of the electrode. There is just a slight decrease of the voltage drop in the upper part during the pulse. This is equivalent to a nearly constant reaction current leaving the electrode in the upper part. So the charge acceptance is much better in the upper

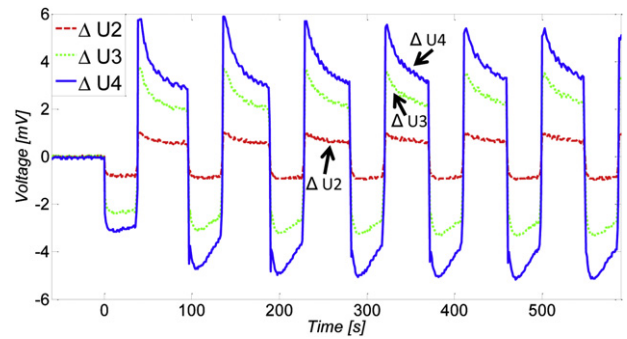


Fig. 12. Voltage drops between different levels during first micro-cycles.

part than it is in the middle and lower regions. Comparing these first charge pulses it is obvious that the lower part is less charged with increasing micro-cycling duration because the voltage drop ΔU_4 decreases. Having a look at a single discharge pulse it becomes obvious that discharging takes place along the whole electrode at the beginning of the pulse and concentrates in upper regions with increasing discharging time. A relatively increasing discharge in the lower region with increasing amount of micro-cycles should be noted as well. This results in the following effect: with increasing micro-cycling duration the lower part gets more and more discharged, because charging of this region decreases and discharging increases with time. This results in a higher degree of discharge in the lower part of the electrode.

Fig. 13 shows the voltage drops of the last micro-cycles. First of all, the results show an increased charge acceptance of the battery. It takes some time until the battery achieves the maximum charging voltage.

The voltage drop at the four levels during the discharge pulses is closer than in the first micro-cycles. This indicates a higher reaction rate in the upper region of the electrode; the lower part is inactive. This is a direct result of the above described phenomenon: the lower part is discharged with increasing amount of micro-cycles and therefore gets inactive.

Fig. 14 shows the voltage drops between different levels. Discharging starts in upper regions and the reaction zone moves down to the middle part with increasing discharge time. There is nearly no discharge of the inactive lower part.

The duration of the Ah-balanced charging pulses decreases in comparison to the first micro-cycles. Two phases can be distinguished during one pulse: a nearly constant voltage drop in the first part caused by a constant charging current followed by a decreasing voltage drop caused by a decreasing charging current during voltage limitation (Fig. 13). Electrochemical reaction takes place in all regions of the electrode at the beginning of the charging. The

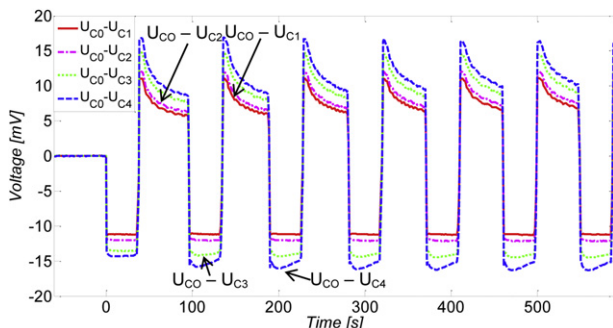


Fig. 11. Voltage drops at different levels during first micro-cycles.

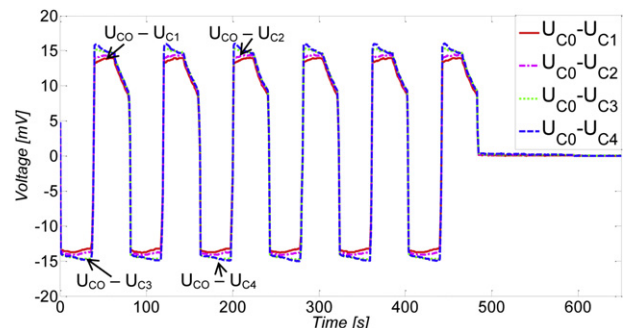


Fig. 13. Voltage drops at different levels during last micro-cycles.

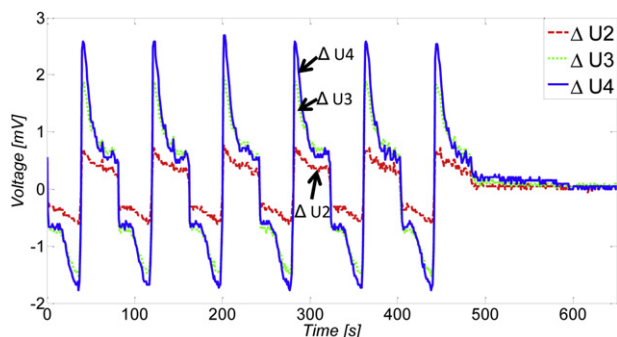


Fig. 14. Voltage drops between different levels during last micro-cycles.

reaction zone moves quickly to the upper region as can be seen in Fig. 14, most of the time almost all charge throughput takes place in the upper part of the electrodes.

In conclusion, micro-cycles have two major effects in this case of preconditioning:

- Dynamic Charge Acceptance increases with the amount of micro-cycles
- The lower part of the electrodes gets more and more inactive in the charging/discharging processes. Post mortem analysis of batteries after several thousand micro-cycles shows string sulphation in the lower part of the electrodes. This is in line with findings on the current distribution.

The measurement technique gives us a good indication on what happens to the current distribution with different operating modes. The findings are in very good agreement with results of post mortem analysis of SLI batteries in stop/start batteries with regenerative braking. The lower parts of the electrodes get inactive during micro-cycling and heavy sulphation takes place.

4. Conclusion

A micro-controller based measuring device has been developed and methods for the determination of acid densities at different levels and the current distribution in the negative electrode have been explained. Results of first measurements validate both methods and motivate further experiments.

It has been shown, that different processes (e.g. gassing) during charging and discharging of an SLI battery can be identified by measuring the spatially resolved acid densities. Measurements of potential distribution during micro-cycling showed a decreasing

dynamic charge acceptance as well as a more and more inactive lower region of the negative electrode with increasing amount of micro-cycles.

5. Further work

Further investigations concerning the acid stratification measurement will concentrate on optimization of measurement accuracy and minimisation of dead-times. The formation process of the sensors will be investigated in detail and procedures similar to the Plante process will be in the focus of interest. A mobile version of the data acquisition tool has already been developed, which allows to measure acid stratification in starter batteries of vehicles during operation.

The resolution of the current distribution measurement will be increased by a higher amount of electrical contacts to the grid. These contacts will be placed on both sides of the electrode and also on its top, so that the equipotential lines can be investigated and be considered for more precise interpretations. Results will be used to optimize a simulation model.

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